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Internal friction in ceria ceramics doped with alkali earth metal oxides

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Abstract

Ceria and 5 mol% of alkali earth metal powder were fired at 1673 K for 6 h in air in order to prepare specimens containing a solid solution of ceria and alkali earth metal oxide. The internal friction as a function of temperature shows a peak at around 450 K. The internal friction peak intensity observed is strongly dependent on the kind of dopant cation. The peak for ceria doped with CaO was the largest, whereas the peak for ceria doped with BaO was the smallest. The ion motion and structures have been analysed by molecular dynamics calculations using as pair potential the Busing approximation of the Born–Mayer–Huggings type. The directions of motion and velocity distributions of dopant cations and oxygen ion vacancies formed by addition of alkali earth metal oxide tend to unidirectional motion and sharp distributions when the ionic radius of the dopant cation is larger or smaller than that of the cerium ion. It is concluded that the internal friction peaks depend on the direction of motion and velocity distribution of the ions.

1. Introduction

The observation of internal friction peaks as well as high ionic conductivity of solid electrolytes such as zirconia-based solid solutions due to doping is associated with the occurrence of oxygen ion vacancies [1]. Ceria doped with alkali earth metal oxides show ionic conductivity associated with oxygen ions [2]. The internal friction of solid electrolytes has been studied by Nowick and coworkers [3–6]. The cerium atoms of valence 4 in ceria by alkali earth metal atoms of valence 2. As a result, some oxygen ion vacancies are formed in ceria. The cation and anion motion in ceria may be varied depending on the concentration and ionic radius of dopant ions [7, 8]. In order to understand better the ion movement in ceria doped with alkali earth metal oxide, it is important to study the ion motion in the vicinity of dopant ions.

Molecular dynamics (MD) calculations have been done by Kawamura and coworkers [9, 10] in order to study the structure of glasses, melts and crystals. MD calculations give much information on crystal structure, atom motion, bond angle and velocity distribution of ions which is difficult to obtain directly from experiment [9].

In the present study the dependence of internal friction peaks on the ionic radius of dopant ions has been compared with the motion of ions calculated by the molecular dynamics method.

2. Experimental procedure

2.1. Sample preparation and internal friction measurement

Ceria and 5 mol% of alkali earth metal oxide powder were mixed in ethyl alcohol by ball milling. The mixed powder was then fired at 1273 K for 3 h in order to produce a solid solution of ceria and alkali earth metal oxide. The calcined powder was crushed in a mortar. To prepare specimens, the crushed powder was fired at 1673 K for 6 h in air. Measurements of internal friction as a function of temperature and frequency were done by the torsion pendulum and flexural vibration method in the temperature range between room temperature and 700 K and the frequency range between 10 Hz and 10 kHz. Activation energies were obtained from the frequency dependence of the peak temperatures and the halfwidths of the peaks.

2.2. Molecular dynamics calculations

The MXDORTO programme of Katsuyuki Kawamura was used for the MD calculations. As pair potential the Busing approximation of the Born–Mayer–Huggings type [10] was used. This potential was chosen because it is simple and it has been demonstrated that structures of oxide crystals and glasses can be reproduced using it. The pair potential is described by

$$\phi_{ij}=f_0(b_i+b_j)\exp\left(\frac{a_i+a_j-r}{b_i+b_j}\right)+\frac{Z_iZ_je^2}{4\pi\epsilon_0 r}$$

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TABLE 1. Values of parameters used in MD calculations

Ion	a_i	b_i	w
Mg	1.161	0.080	24.31
Ca	1.440	0.080	40.08
Sr	1.632	0.080	87.62
Ba	1.820	0.080	137.33
Ce	1.521	0.080	140.12

w, atomic weight.

where r is the distance between atoms, ϵ_0 is the dielectric constant, e is the electron charge, Z_i is the valence of the ith atom, $f_0 = 6.9472 \times 10^{-11}$ N and a_i and b_i are potential parameters related to the size and compressibility of the ith atom respectively. The potential parameters of each atom were determined empirically by reproducing two or more well-known crystal structures. The values of the parameters are listed in Table 1. Three-dimensional periodic boundary conditions are assumed for basic cells containing 96–324 atoms. The basic cell, which has eight unit cells or 27 unit cells, contains one dopant ion in the middle and one oxygen vacancy induced by replacing one oxygen ion which is nearest neighbour to a dopant ion by a vacancy. The equation of motion was integrated at time intervals of 2×10^{-15} s. A constant pressure of 0.0001 GPa and constant temperatures of 300, 500 and 1273 K were chosen and the systems were kept at each temperature for 1×10^{-12} s.

3. Results

The internal friction peaks for ceria doped with MgO, CaO, SrO and BaO are shown in Fig. 1. The internal friction has small values at room temperature and becomes maximum at about 450 K for all samples. The internal friction peak strength for ceria doped with MgO is the smallest of all samples investigated. The temperature and halfwidth of the peak are 422 K and 55 K respectively, as shown in Fig. 1. The internal friction peak for ceria doped with CaO is the largest of all samples. The peak value is 4.2×10^{-3}. The temperature and halfwidth of the peak are 430 K and 113 K respectively. The internal friction peak strength for ceria doped with SrO is smaller than that for ceria doped with CaO. The intensity and halfwidth of the internal friction peaks are strongly affected by the type of dopant ions, as shown in Fig. 1.

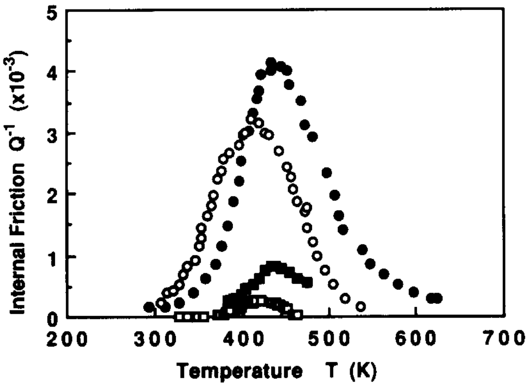

Fig. 1. Temperature dependence of internal friction in ceria doped with 5 mol% MgO (□), CaO (●), SrO (○) and BaO (■). Measurement frequencies are 3110, 2450, 2010 and 8410 Hz respectively.

TABLE 2. Comparison of activation energies of internal friction peaks calculated from Arrhenius equation and peak halfwidths

Activation energy	Dopant (5 mol%)			
	MgO	CaO	SrO	Ba
H_a (kJ mol^{-1})	92	131	86	79
H_w (kJ mol^{-1})	71	35	33	70

The activation energy H_a can be calculated from the Arrhenius equation

$$\ln \omega = \frac{-H_a}{R(1/T_p)} - \ln \tau_0$$

where T_p is the peak temperature, $\omega = 2\pi f$, R is the gas constant and τ_0 is the relaxation time. For a single-time process the activation energy H_w can be calculated from the peak halfwidth using the following equation

$$H_w = \frac{2.63RT_1T_2}{T_2 - T_1}$$

where T_1 and T_2 are the temperatures of the half-maximum of the internal friction peak.

Table 2 gives a comparison of the activation energies of the internal friction peaks calculated from the Arrhenius equation and the peak halfwidths. H_a for ceria doped with MgO is nearly equal to H_w. However, H_a for ceria doped with CaO is larger than H_w. The difference between H_a and H_w was minimum for ceria doped with CaO.

The peak for ceria doped with CaO contains at least three independent single-relaxation contributions, as shown in Fig. 2. The temperatures of the peaks are 400, 433 and 490 K respectively. The halfwidth of each peak is about 65 K.

4. Molecular dynamics calculations

The atomic motions in ceria with a dopant and a vacancy are shown in Figs. 3 and 4. Motion traces are indicated in the lattice. The directions of motion of vacancies and dopant ions in ceria doped with MgO

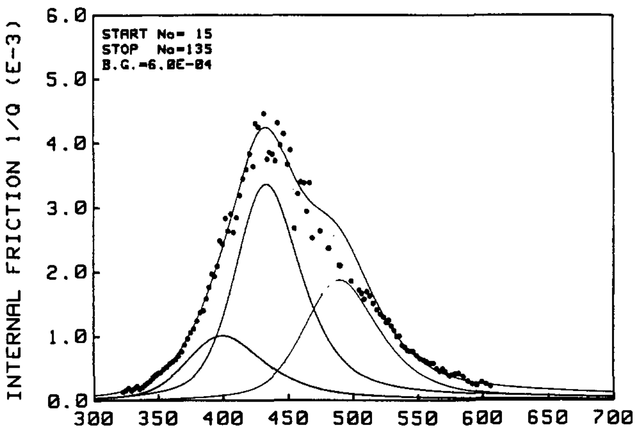

Fig. 2. Components of internal friction peak for ceria doped with 5 mol% CaO. Three peak components are calculated from the experimental data.

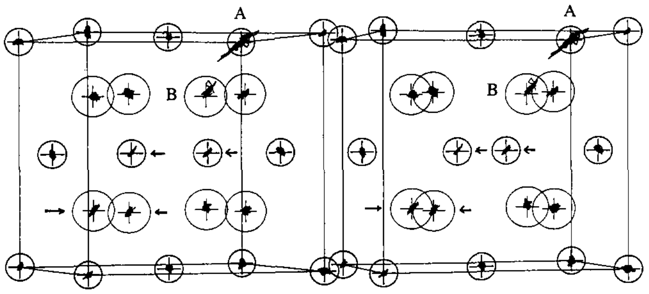

Fig. 3. Stereoscopic pair drawing of ion motion in fluorite unit cell of ceria doped with MgO: A, dopant cation; B, vacancy; small circles, O ions; large circles, Ce ions. As indicated by the arrows, Ce ions and O ions move unidirectionally.

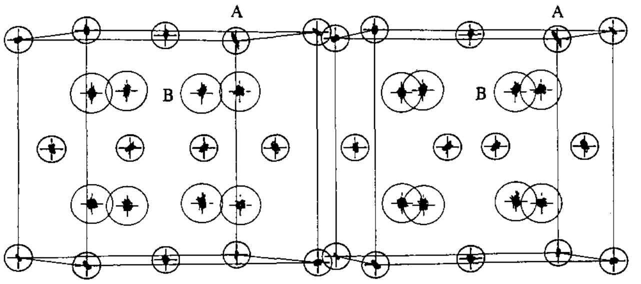

Fig. 4. Stereoscopic pair drawing of ion motion in fluorite unit cell of ceria doped with CaO: A, dopant cation; B, vacancy; small circles, O ions; large circles, Ce ions. Ce ions and O ions move uniformly.

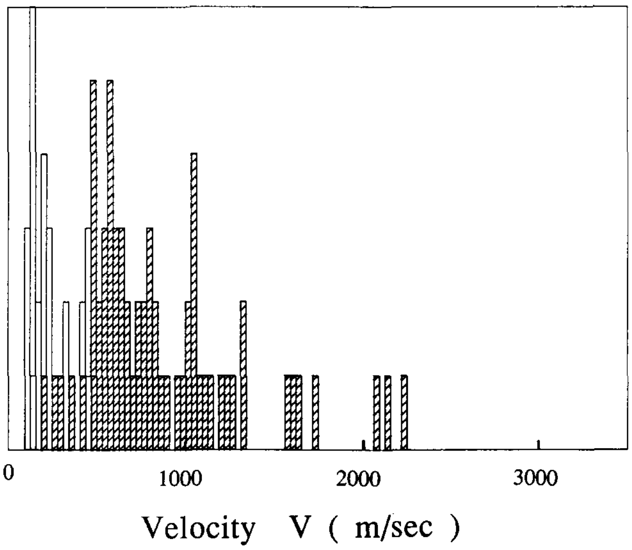

Fig. 5. Velocity distribution of O ions (hatched) and Ce ions (white) in ceria doped with MgO.

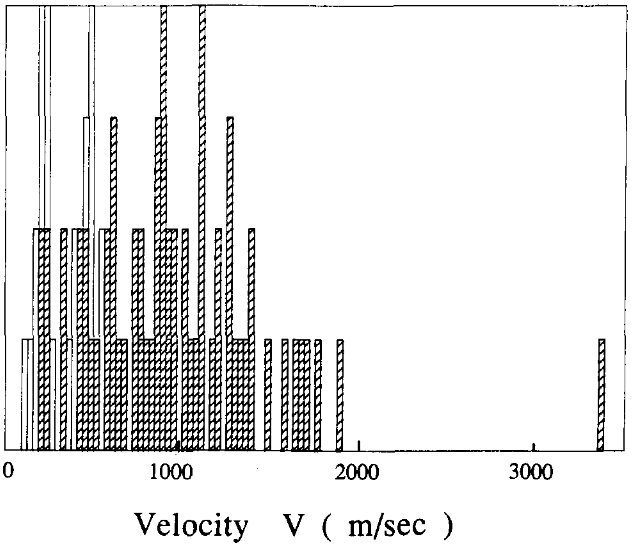

Fig. 6. Velocity distribution of O ions (hatched) and Ce ions (white) in ceria doped with CaO.

are distributed unidirectionally, as shown in Fig. 3. In the case of ceria doped with CaO the dopant ion and vacancy motions are distributed in a wide range of directions, as shown in Fig. 4.

The velocity distributions of oxygen and cerium ions in ceria doped with MgO and CaO are shown in Figs. 5 and 6. The velocities of oxygen ions in ceria doped with CaO show a wide distribution, whereas their velocities in ceria doped with MgO show a narrow distribution.

5. Discussion

The mechanism of internal friction of the relaxation type is related to the Snoek relaxation. The mechanism of internal friction in solid electrolytes such as ceria doped with Sc_2O_3 has been discussed from the point of view of the displacement of an oxygen ion due to the effect of the substitutional scandium ion using computer simulation [2].

The halfwidth of the peak depends on the distribution of relaxation times. The difference in peak shape between ceria doped with MgO and with CaO will be discussed using MD computer simulation as follows.

As shown in Fig. 2, the internal friction peak for ceria doped with CaO has three components, while the peak for ceria doped with MgO has only one. In fact, for the latter H_a and H_w were similar and the same is true for ceria doped with BaO, in which the barium ion has a larger ionic radius than the cerium ion. This means that the relaxation of ceria doped with MgO and BaO is due to one mechanism, whereas the relaxation of ceria doped with CaO involves three different mechanisms.

MD calculations of the motion of oxygen and cerium ions indicate that the motion in ceria doped with MgO is unidirectional. The distribution of the directions of ion motion becomes narrow when the ionic radius of the dopant ion is smaller or larger than that of the cerium ion. The motion of an oxygen ion which is nearest neighbour to a vacancy is slightly anisotropic in the case of BaO-doped ceria. On the other hand, when ceria is doped with CaO, the oxygen ion moves uniformly, as shown in Fig. 4.

Figure 5 shows the velocity distribution of oxygen ions in ceria doped with MgO. The mean value of the velocity is about 800 m s^{-1} and the width of the distribution is about 900 m s^{-1}. The mean value and width in ceria doped with CaO (Fig. 6) are 1000 m s^{-1} and 1500 m s^{-1} respectively. The 490 K peak is observed in ceria doped with CaO but not in ceria doped with MgO. The high velocity component of the velocity distribution calculated by MD is larger in ceria doped with CaO than in ceria doped with MgO. The internal friction peak observed at a higher temperature means that the oxygen ion motion and relaxation process are faster than in ceria itself, which has an internal friction peak at a lower temperature. This fast oxygen ion motion and relaxation process can be related to the higher velocity component of oxygen ion motion calculated by MD. The width of the velocity distribution can be related to a broader scattering of relaxation times. The direction of motion of ions becomes unidirectional when the ionic radius of the dopant is larger or smaller than that of the cerium ion. This may also be helpful in explaining the decrease in breadth of scattering of the relaxation process.

6. Internal friction peak strength

The velocity of an oxygen ion which is nearest neighbour to a vacancy is extremely high, as shown in Fig. 6. This means that an oxygen ion which is nearest neighbour to a vacancy formed by substitution of calcium ions can move more easily than an oxygen ion which is nearest neighbour to a vacancy formed by substitution of magnesium ions. Comparing the traces of the oxygen ion motion, the motion in ceria doped with CaO is stronger than in ceria doped with MgO.

The higher intensity of the internal friction peak for ceria doped with CaO can also be explained by the higher oxygen ion mobility.

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